NONEQUILIBRIUM CLUSTER FORMATION IN ROCKET EXHAUSTS

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13. ABSTRACT

Crude estimates of cluster-forming kinetics based on molecular beam measurements and scaling methods indicate that very large polymers ($0\ 10^{10}$) will form in the vacuum plumes of large rocket engines. Although no scaling methods exist that are properly applicable to polyatomic species, we have applied the monatomic species scaling concepts developed by Hagena, et al, to the molecular parameters of the H_2O molecule in order to estimate its clustering behavior. These calculations indicate that the products of adiabatic combustion of H_2 and O_2 will form clusters of several thousand H_2O molecules if allowed to expand freely to vacuum, and if the product $p_o d^{.6}$ 170 atmcm$^{.6}$, where p_o is the stagnation pressure and d is the throat diameter. The parameters of rocket engines of interest are greater than this, so the expectation would be that numerous clusters will form with a mean diameter of 100A or more. An examination of the growth laws in the far field of the rocket plume shows that an additional growth mechanism that is negligible for the conditions of the existing experiments produces a subsequent gain of $0\ 10^{2}$ beyond these projections, giving a final estimated particle size of the order of 1 for the SIVB rocket case. Several experiments that could be performed to define the basic cluster-forming rates, cluster size distribution and to confirm the scaling relationsbips are discussed. These experiments include the use of plumes from a perfectly mixed combustion simulating a variety of rocket propellants at various scale sizes.

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INTRODUCTION

For over ten years research on condensation in high intensity molecular beams has been pursued actively by several groups[1-4]. Large clusters have been detected in a variety of gases, expanding through different types of nozzles, from many different source temperatures and pressures. Hagena et al.,[5] and Hagena and Obert[6], in their pioneering works on scaling laws for cluster formation, have succeeded in correlating results for a large body of experimental data. This work is based on the principle that the same condensated clusters will result from "corresponding jets", i.e., jets that are totally similar in terms of the controlling molecular processes. In the case of the noble gas family, they have been able to collapse the data of different gases to a single curve. Polyatomic species are considerably more difficult to treat because of their internal degrees of freedom, but some progress has been made in correlating experiments in CO_2 and N_2.

Because of experiments, it is possible to predict the occurrence of very large clusters in the exhausts of rocket engines. The approach is semiempirical in that it relies upon experimental data instead of on an a priori theory. As such, confidence in the predictions increases uniformly as the conditions of the experiments approach those of the actual applications. The present predictions are very crude because the available data deal with (in approximate order of importance) different gases, lower stagnation temperatures, lower pressures, very much smaller nozzles, very pure single component flows and polyatomic species (for which the scaling laws are less well developed than for monatomic). This situation offers an opportunity to conduct more definitive experiments to obtain a much firmer foundation for predicting cluster formation in rocket exhausts.

In spite of the large degree of extrapolation in the preliminary estimates made in the following section (Analysis), the margin between the conditions for cluster formation and those of typical rockets makes the existence of very large clusters quite probable. The semiempirical approach advanced is completely compatible with, but separate from, the calculation of nucleation and growth using classical condensation theory applied to the conditions of a nozzle expansion. It is expected that both approaches would be pursued simultaneously.

ANALYSIS

The calculations in this section rest on the methods and data presented by Hagena and Obert[6]. No attempt is made here to describe or analyze their methods in detail, as Ref. 6 presents that information. Our confidence in the validity of the work in Ref. 6 is very high, based on a close association with Dr. Hagena dating from 1964.

Data are presented in Fig. 1 taken from Ref. 6 for Ne, Ar, Kr, and Xe, showing the reduced stagnation pressure, $\overline{p_o} = p_o \sigma^3/\epsilon$, vs the reduced stagnation temperature, $\overline{T_o} = T_o \kappa/\epsilon$, necessary to produce a mean cluster of 3500 atoms in a conical nozzle with a reduced throat diameter, $\overline{d} = d/\sigma = 4 \times 10^5$ and a reduced nozzle length, $\overline{L} = L/\sigma - 7.2 \times 10^7$. The parameters σ and ϵ are the equivalent Lennard-Jones 6-12 potential parameters of atomic diameter and well depth, respectively. In all Fig. 1 displays 11 different test conditions involving the 4 noble gases as a straight line in logarithmic coordinates. It is apparent that the correlation technique works quite well.

Hagena and Obert[6] also show comparable results for forming clusters with a mean number/charge ratio of 10^3 for noble gases, for CO_2, and for N_2. We have replotted their data in Fig. 1, using the same molecular scaling approach as was used by Hagena and Obert to correlate the noble gas data, and making the arbitrary assumption that the polyatomic species cluster will have the same number/charge ratio as Ar; $(N/Z)^* = 1000$ yields 3500 molecules/cluster. It is quite apparent that the differences between the polyatomic gases N_2 and CO_2 are small, but they differ somewhat (about 6 fold higher normalized pressure at high $\overline{T_o}$) from the noble gas family in this similarity variable coordinate system. For present estimates, we will use the extrapolation of the polyatomic data indicated by the dashed line in Fig. 1.

Although no one, to our knowledge, has investigated cluster formation with H_2O using the same techniques as Hagena and Obert, we can make an estimate of the cluster sizes using the extrapolation in Fig. 1. Monchick and Mason[7] give recommended values of the Lennard-Jones 6-12 parameters for H_2O as $\sigma = 2.71$A and $\epsilon/k = 506^\circ$K. Hydrogen-oxygen rocket engines, such as the Apollo SIV B engine, operate at chamber temperatures of about 3500°K, but we have based our calculations on a stagnation temperature of 4000°K to account for the extra energy in vibration and dissociation that is present in the rocket, but not in the molecular beam data. This leads to a reduced temperature of 7.9. From the extrapolated curve, this value produces a reduced pressure of 0.75. The factor ϵ/σ^3 is 3470 atm for H_2O. Because the polyatomic species will be more likely to form multiply charged

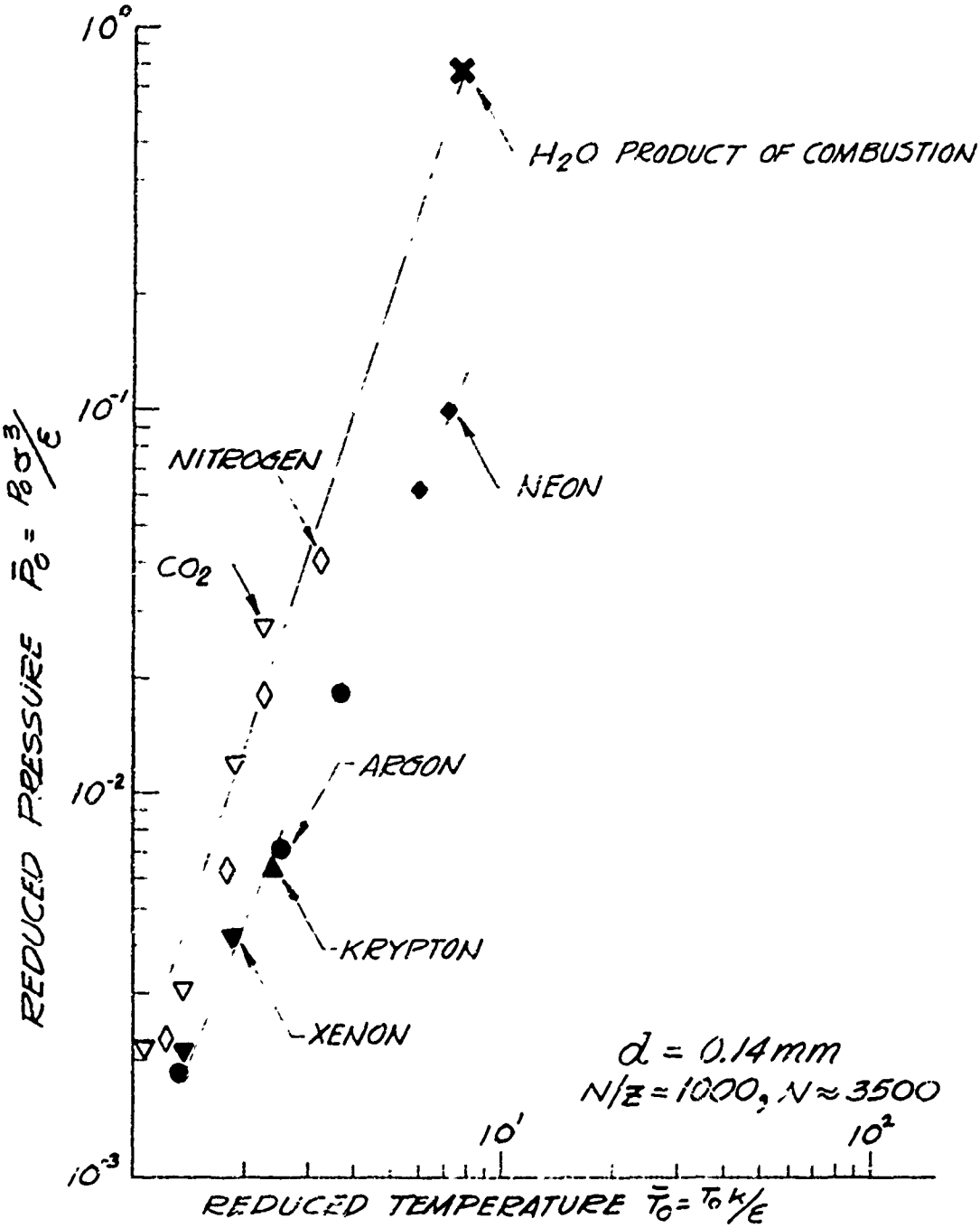

Fig. 1 Corellation of Cluster Data (After Hagena & Obert[6]) Showing Extrapolation to 4000°K H2O

clusters, we would expect that this value of the reduced pressure will produce a mean cluster size considerably greater than the 3500 value to which $(N/Z)^*$ corresponds in argon.

To place this value of $\overline{p_o}$ in perspective, it must be remembered that this value corresponds to a reduced throat diameter, for which the data were plotted, of 4×10^5. The reduced diameter, $\bar{d}$, produces a reference diameter of 0.0108 cm for H_2O. As an illustration of the technique, we shall consider the case of the SIV B engine which has a throat diameter of approximately 39 cm. The work of Hagena and Obert[6] indicates that a constant characteristic specific cluster size, $(N/Z)^*$, results when $p_o d^q$ = constant (for constant stagnation temperature and the same pure species) with $q = 0.6$ for CO_2. Hence, for the H_2O conditions of Figure 1 we get $p_o d^{.6} = 174$ ATM-cm$^{.6}$ which corresponds to $(N/Z)^* = 1000$ or $N = 3500$. For the Apollo SIVB engine the corresponding value of $p_o d^{.6}$ is 444 ATM-cm$^{.6}$. In Ref. 8, figure 8, Bauchert and Hagena show the variation of $(N/Z)^*$ for CO_2 as a function of d with p_o as parameter and T_o held constant. A crossp ot of these data indicates that $N/Z \sim \left(p_o d^{.6}\right)^{3.5}$. Thus, a lower limit to the expected mean H_2O cluster in the SIV B engine exhaust plume would be (3500 atms/cluster) $\times \left(\frac{444}{174}\right)^{3.5} \cong 10^5$ atoms per cluster. This is equivalent to particles with a mean diameter of 180Å if each H_2O molecule is assumed to occupy a cube of $2^{1/6}\sigma$ on a side.

One major factor that we cannot evaluate quantitatively at all is the effect of diluent gases. The literature on molecular beam condensation experiments repeatedly characterizes the effects of impurities as being important[6], but does not indicate whether they systematically increase or decrease the sizes of clusters. In rocket engines the H_2O molecule will be mixed with generous amounts of O, H, O_2, H_2, N_2, OH, CO_2, CO, etc. The effects of these diluents will be extremely important and may result in either enhancement or inhibition of cluster formation. Lacking any good rule for applying corrections, we have neglected the effects of diluents. However, any experiments aimed at understanding the formation of H_2O clusters in a rocket plume in space should include the effects of all possible species, each at the proper energy.

The experiments and scaling laws of Hagena and Obert[6] were developed after experimentally determining that further growth did not occur downstream of the sampling station. We now examine the cluster growth termination in a plume of a

rocket relative so that in the Hagena experiments. In order to do this, we have derived a very simple model of the growth of a large cluster in the far field of a plume.

Let us consider a cluster of size No located at station X_o in a plume that has a monomer number density field $n = .086\, n_o\, (X/d_{eg})^{-2}$ and $M = 3.65\, (X/d_{eg})^{2/5}$; here $d_{eg} = .86 d_{cn}/\text{TAN}\,\theta$ is an equivalent sonic nozzle which produces the same centerline flow properties as a conical nozzle which has throat diameter, d_{cn}, and half angle θ (for $\gamma = 1.4$). The cluster travels with the mean flow velocity U, and monomers collide with the cluster according to the normal kinetics, with an effective cluster cross section Σ. If we neglect sublimination, assume that every monomer sticks to the cluster, and estimate that $\Sigma \approx \sigma\, N^{2/3}$, where σ is the cross section for monomer-monomer collisions; we get the following expression for the growth in cluster number:

$$\frac{dN}{dx} = 8 \times 10^{-3} \sqrt{\frac{1}{2\pi\gamma}}\, \sigma_o\, N^{2/3} \left(\frac{x}{d_{eg}}\right)^{-2.4}$$

this equation can be integrated to give

$$N^{1/3} - N_o^{1/3} = 1.9 \times 10^{-3}\, n_o\, \sigma_o\, d_{eg}^{2.4} \left[\left(\frac{1}{x_o}\right)^{1.4} - \left(\frac{1}{x}\right)^{1.4}\right]$$

which becomes

$$\frac{N(x)}{N_o} = \left[1 + \frac{1.9 \times 10^{-3}\, n_o\, \sigma_o\, d_{eg}}{\left(\frac{x_o}{d_{eg}}\right)^{1.4} N_o^{1/3}} \left(1 - \left(\frac{x_o}{x}\right)^{1.4}\right)\right]^3$$

$$\frac{N(\infty)}{N_o} \approx \left[\frac{1.9 \times 10^{-3}\, n_o\, \sigma_o\, d_{eg}}{(x_o/d_{eg})^{1.4}\, N_o^{1/3}}\right]^3 \approx 5\, \frac{d_{eg}^3}{N_o} \quad \text{at } P_o = 720\text{psi}$$

We can now compare the far downstream growth of the Apollo SIV B rocket above that of the Hagena-Obert experiments for identical x_o/d and N_o:

$$\frac{N(\infty)}{N_o} = \frac{5\,(380)^3}{3500} \approx 8 \times 10^4$$

The surprising result is that there is an additional growth of a factor of order 10^5 available in the case of a rocket, but not possible in small-throat

experiments. The scale of this growth is one order of magnitude greater than x_c, and x_o is about 30 d_{eg} in the Hagena experiments. In the SIVB rocket engine this growth takes place over a large fraction of a kilometer. Obviously, the factor of 10^5 is an overestimate, because depletion of monomers, evaporation and less than unity sticking would be important, but that value would correspond to a mean cluster size of about 1 μ if it were all realized. Clearly, the observed case of micron-sized particles is explainable by this effect, especially if one considers the fact that the mean density of a large cluster will be closer to that of snow than to that of ice.

One additional comment on the present model is in order. The phenomenon of translational freezing will occur in the actual expansion and it will serve to increase the downstream growth rate by keeping the effective Mach number (based on the "parallel temperature") lower than the estimate we used. Translational freezing will occur while the large clusters are growing because the large clusters will have cross section orders of magnitude greater than individual particles, so cluster collisions are important long after collisions between monomers are negligible.

The above sequence of extrapolations is obviously not accurate to within an order of magnitude unless we have been extremely fortunate. Its results are consistent with observations, however, and it is particularly well suited to systematic improvement. The following section describes a set of experiments that will provide a fresh data base upon which these scaling concepts can be reapplied. When results are taken using H_2O and a systematically controlled set of diluents generated by combustion at elevated pressures and with different sized nozzles, these scaling laws should be extremely accurate when used to bridge the (then) relatively small gap between laboratory and flight conditions.

EXPERIMENTS

The objective of the investigation would be to determine by experiment the characteristics of, and the scaling laws for, the nucleation of water vapor in the exhaust plume of a rocket. The experimental approach is in the spirit of that applied by Hagena and Obert[6]. High energy water vapor plumes, with and without diluents, are generated in our plume simulator. The plume flow field is then mass analyzed by forming a molecular beam that is passed through an electron bombardment ionization gauge that has a retarding potential field ion collector. The measured ion signals, as a function of retarding potential, provide a direct measure of the specific cluster size of the ions, N/Z, where N is the number of atoms or molecules in the cluster and Z is the number of charges. By measuring the cluster ion size as a function of electron energy (ionization cross section depends on electron energy) it is possible to infer the mean neutral cluster size. In addition, this detector can provide other information of practical interest such as the cluster beam velocity and number density that can be used to obtain the cluster mass flux density. In this section we describe briefly the experimental apparatus, anticipated operating conditions, and the required modification to our existing electron bombardment detector (EBD).

A schematic diagram of the Grumman plume simulator (Refs. 9, 10) is shown in Fig. 2 indicating the location of an EBD and the elements (skimmers) that are required for molecular beam formation. The operation of this facility is similar to that of a conventional reflected shock tunnel, the major difference being that the driven tube is loaded with a combustible mixture of gases so that either the incident or reflected wave becomes a detonation. The flow process is initiated when a shock wave is generated by rupture of the double diaphragm. Depending on the strength of the incident shock and the initial conditions of the gas mixture, it is possible to cause ignition by either the incident shock wave or by the shock wave that is reflected at the nozzle location. The choice of initial mixture and ignition mode depend upon the plume simulation requirements. For example, when H_2/O_2 propellant systems are considered, reflected shock ignition will produce the enthalpy condition corresponding to the real rocket engine case[10]. On the other hand, simulation of the Lunar Module reaction control engines (Nitrogen tetroxide and Aerozene 50) require incident shock wave ignition to produce the correct enthalpy condition[9].

The H_2/O_2 system will be used in our initial experiments, with a wide variety of O/F ratios, so that controlled concentrations of the diluents (O, H_2, O_2, OH, etc) can be obtained. Although the facility is structurally capable of operating at stagnation pressures up to 20,000 psi, our present capability is limited by ignition reliability to about 2500 psi.

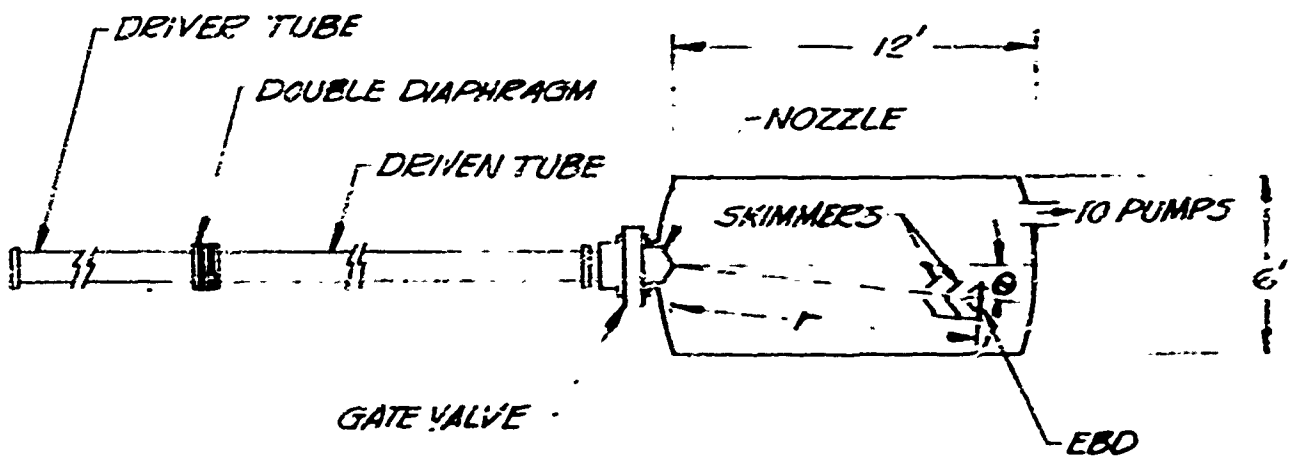

Fig. 2 Schematic Drawing of Plume Simulator Setup for Nucleation Investigations

Development work to improve this capability is now in progress under NASA contract NAS 9-12447. The proposed investigation should include a family of geometrically similar conical nozzles, with throat diameters up to 1 cm. The upper limit of the present range of stagnation pressures and nozzle diameters corresponds to, for example, 0.1 of the full scale Reynolds number of the Apollo SIVB rockets. These test conditions will be supplemented with the N_2O_4 + aerozene 50 simulations. For such tests NH_3 clusters could be a factor, so some NH_3 shock runs may also be investigated.

The plume flow field is started impulsively when stagnation conditions at the nozzle location are established behind the reflected wave (shock or detonation). The reactants flow into the vacuum chamber where a steady state plume exists for several milliseconds. At the skimmer location (Fig. 2), the local flow properties of interest are obtained by forming a small segment of the plume into a molecular beam and passing the beam through the EBD.

Molecular beam sampling of shock tube generated flow fields should present no significant problem because of our previous experience during the development stages of a shock tube driven molecular beam facility[11]. The multiple collimation scheme shown in Fig. 2 ensures the formation of a molecular beam sample that has the local free stream properties exclusive of collision products that are usually produced when a high intensity molecular flow field interacts with the skimmers[11]. Note that it is unnecessary to provide a separate evacuation system for the skimmers because of the short flow duration. The skimmers will be built into a modular assembly that includes an EBD gauge. The resulting system will be supported in the vacuum chamber so that it can easily be traversed axially as well as rotated in a plane of symmetry of the axisymmetric nozzle, the rotation being along a circular arc centered in the nozzle exit plane. With this flexibility the cluster distributions can be determined as a function of both γ and Θ (see Fig. 2). We expect that the distribution of cluster size will be significantly different off axis because of mass separation effects; the centerline flux distribution should have a higher percentage of large aggregates, especially for downstream.

Our basic detection method will employ an ionization gauge of the type originally developed by Hagena and Henkes[12]. In this detector, a narrow ribbon of electrons is accelerated to 100 eV and allowed to pass perpendicularly to the flux of molecules which enter the gauge through the conical inlet. Positive ions are formed in proportion to the local instantaneous number density of the neutral molecules and are collected downstream of the electron sheet on a fine cylindrical probe. We have determined the nominal sensitivity of these detectors in chopped effusive beams to be 10^{-12} microamps of ion current for 1 argon

atom/cm^3, with 1 milliamp of electron current. The sensitivity of the gauge to some other gas, say N_2, can be determined from the ionization cross section of the gas at the appropriate electron energy.

By a simple change in collector geometry, the addition of a control electrode between the ion collector and the electron beam, it is possible to make the ion collector energy sensitive[8]. Actually, several electrodes may be used in order to establish a uniform retarding potential across the entire ion beam. With the ion collector at fixed potential, a positive voltage, V_c, is applied to the control electrode so that a retarding potential, V_R, is established. Under these conditions, the kinetic energy of the ions reaching the collector must satisfy the inequality;

$$E_N = \frac{1}{2} NMV^2 > Ze V_R$$

where E_N = the kinetic energy of a Z times charged cluster
N = number of atoms or molecules in the cluster
M = mass of a molecule
V = mean cluster velocity ≈ mean velocity in the flow field
e = electronic charge

For water vapor, assuming a mean flow velocity of 3000 meter/sec., we obtain the following relationship for the minimum specific ion cluster ratio (N/Z)* reaching the collector.

$$(N/Z)^* \approx V_R/1.15 \text{ volts}$$

To obtain the cluster size distribution, the ion current i^+ must be measured as a function of V_R. In our experiments we intend to apply a ramp voltage $V_c(t)$ to the control electrode, so that V_R will range between 0 and 1.15 (N/Z)* volts on a 1 millisecond time base. The upper voltage level employed depends on the maximum size of the anticipated clusters, e.g., for a cluster size of 1000, $V_{R_{max}} = 1,150$ volts. A rough sketch of the anticipated signal shape for a typical run is shown in Fig. 3.

The maximum ion signal level i^+ max, with $V_R = 0$, is a direct measure of the total particle density at the detector location. When $V_R(t)$ is applied, sometime after quasi-steady state conditions are achieved, three possible variations of i^+ are indicated; corresponding to maximum cluster sizes $(N/Z)_{max}$ less than $V_{R_{max}}$ (a), equal to $V_{R_{max}}$ (b) and greater than $V_{R_{max}}$ (c). In the first two cases, the mean specific ion cluster size is obtained at $i^+(V_R)/i^+(V_R=0) = .5$. If case c occurs, the maximum ramp voltage will have to be increased before the mean can be evaluated.

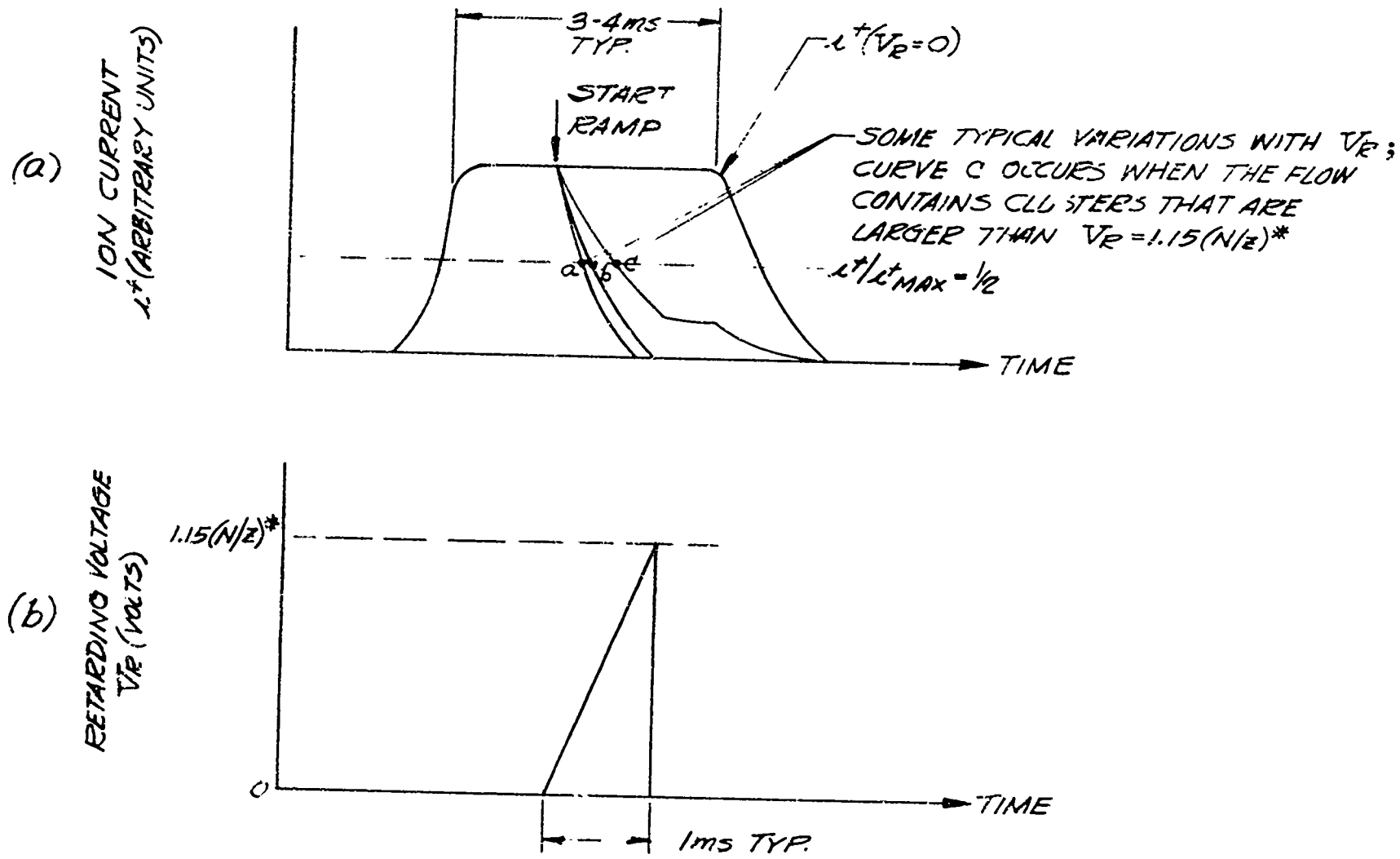

Fig. 3 Expected Signal Characteristics from a Retarding EBD (a), When a Ramp Retarding Voltage is Applied to the Control Electrode (b)

The above procedure gives an unequivocal measure of the specific size distribution, f(N/Z). The final problem is to relate this distribution the the distribution of absolute size, f(N). First, the simple assumption of one unit charge on every cluster sets a reliable lower limit to any measure of cluster size, e.g. $\overline{N}_{min} = \overline{N/Z}$, etc. Beyond this, various methods of estimating the charge distributions on the clusters can be used. Hagena and Obert[6] quote direct measurements in Ar and Xe, and extrapolations for Ne and Kr that give effective mean charges per cluster of 1.5 for Ne, 3.5 for Ar, 4.4 for Kr, and 4.7 for Xe; all at a mean N/Z of 1000. The need for inferential determination of cluster charge distribution is clearly a problem if accurate values of number distributions are required, but for setting a firm minimum cluster size with an estimate of actual size based on solid density and ionization cross section of the individual molecule, present methods are acceptable. In all probability the molecular clusters CO_2, NH_3 and H_2O produce effective $\overline{Z}$ values closer to 10 than to unity.

CONCLUSIONS

We have shown that the best estimate from available data and known scaling rules predicts the formation of large numbers of H_2O clusters in the vacuum plumes of large rockets. The mean size of these clusters is probably greatly in excess of 10^4 A^o, although it is not possible to predict mean size with any degree of accuracy. We have described a series of experiments that could be performed in our rocket plume simulator to determine the cluster forming characteristics and scaling rules of real rocket flows. The experiments do not involve any techniques other than those routinely used in our laboratory or in the Kernverfahrenstechnik Institute at Karlsruhe, W. Germany.

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